

# Complexation thermodynamics and structural studies of trivalent actinide and lanthanide complexes with DTPA, MS-325 and HMDTPA

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**Summary.** The protonation constants of DTPA (diethylenetriaminepentaacetic acid) and two derivatives of DTPA, 1-R(4,4-diphenyl cyclohexyl-phosphonyl-methyl diethylenetriaminepentaacetic acid (MS-325) and (R)-hydroxymethyl-diethylenetriaminepentaacetic acid (HMDTPA) were determined by potentiometric titration in 0.1 M NaClO<sub>4</sub>. The formation of 1 : 1 complexes of Am<sup>3+</sup>, Cm<sup>3+</sup> and Ln<sup>3+</sup> cations with these three ligands were investigated by potentiometric titration with competition by ethylenediaminetetraacetic acid (EDTA) and the solvent extraction method in aqueous solutions of *I* = 0.10 M NaClO<sub>4</sub>. The thermodynamic data of complexation were determined by the temperature dependence of the stability constants and by calorimetry. The complexation is exothermic and becomes weaker with increase in temperature. The complexation strength of these ligands follows the order: DTPA ≈ HMDTPA > MS-325. Eu<sup>3+</sup>/Cm<sup>3+</sup> luminescence, EXAFS (Extended X-ray Absorption Fine Structure) and DFT (Density Functional Theory) calculations suggest that all three ligands are octadentate in the complex. In the complex, M(L)<sup>2-</sup> (L = DTPA, MS-325 and HMDTPA). The M<sup>3+</sup> binds *via* five carboxylates oxygen atoms, three nitrogen atoms, and the complex contains one water of hydration.

## 1. Introduction

Aminocarboxylates complexes of lanthanides and actinides are not only interesting because of their chemical and structural properties, but they have an important place in the history of the lanthanides and actinides separation chemistry. Early experiments on separation of lanthanides were carried out in tracer scale using citrate complexes, but attention soon turned to the aminocarboxylates because EDTA and related ligands were found to be more effective [1]. Now, more than half a century after the first use of aminocarboxylates, the study of their complexation with lanthanides and

actinides continues to be a major area in *f*-elements coordination chemistry.

DTPA is a potentially octadentate ligand and forms complexes with larger stability constant of the type M(DTPA)(H<sub>2</sub>O)<sup>2-</sup>. The crystallographic data of Ln(DTPA)<sup>2-</sup> in solid (Ln = lanthanides) [2, 3] and the luminescence lifetime measurements in solution [4, 5] are consistent with the presence of one water of hydration in the inner coordination sphere of Ln(DTPA)<sup>2-</sup>. Additionally, DTPA is a promising chelating agent in lanthanide and actinide separations [6]. In the nuclear fuel cycle, DTPA is used in the separation of trivalent actinides and lanthanides because of their larger separation factors for actinides-DTPA complexes relative to that of the lanthanides-DTPA. The TALSPEAK (Trivalent Actinide-Lanthanide Separation by Phosphorous Extractants and Aqueous Komplexes) separation of trivalent actinides and lanthanides is based on this foundation [7, 8].

Besides effective chelating agents in lanthanide-actinide separation, DTPA is also used as a decontamination agent in individuals who have ingested radioactive materials.

The complexes of lanthanides with DTPA and its derivatives are also very important, because of their use in magnetic resonance imaging (MRI) as a contrast agent [9]. Complexes of Gd<sup>3+</sup> with MS-325 have also received attention as potential contrast agent for MRI currently undergoing clinical trials [10]. It possesses a lipophilic diphenylcyclohexyl group which provides a strong non-covalent binding interaction with the blood plasma protein human serum albumin (HAS). HMDTPA was also designed using the Gd(DTPA)(H<sub>2</sub>O)<sup>2-</sup> (magnevist) core which has an excellent human safety record [11, 12]. It was expected that substitution on the ethylene backbone would not adversely affect the thermodynamic stability nor kinetic inertness of the complex.

Since the properties of *f*-cation complexes are determined principally by ionic and steric effects, comparison of the complexation of DTPA, MS-325 and HMDTPA with these cations can provide insight into whether the introduction of functional groups in the ethylenediamine backbone enhances the complexation and, also, how the steric dif-

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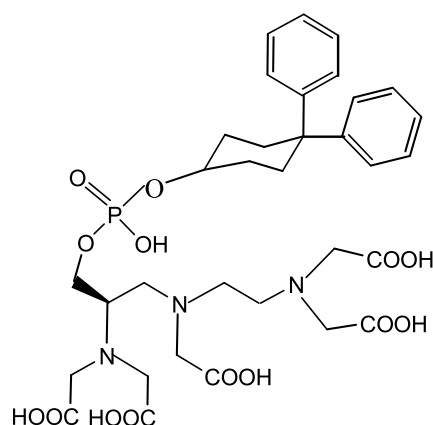
ferences between the flexible DTPA and HMDTPA, and the rigid MS-325 affect the complexation properties. There have been a few studies on the complexation of lanthanides and actinides with DTPA but only at or near 25 °C [13–17]. Thermodynamic constants of their complexation with  $\text{An}^{3+}/\text{Ln}^{3+}$  are still very scarce. Although, the complexation of DTPA with lanthanides and actinides has been studied in the past, the systematic studies on the complexation of other two ligands with lanthanides and actinides have not been investigated. There is only one report in the literature on the complexation study of MS-325 with  $\text{Gd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  at 25 °C in 0.1 M  $\text{NaClO}_4$ . Therefore, in the present study, we initiated a systematic study on complexation of  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ , and  $\text{Ln}^{3+}$  with DTPA, MS-325, and HMDTPA. Ligands protonation constants and their stability constants with  $\text{Ln}^{3+}$  were measured by potentiometric titration method (direct pH titration and competition with EDTA, respectively), while solvent extraction technique was used to determine the stability constants with  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ . The associated thermodynamic data of these complexes were measured either by micro-calorimeter or by temperature dependence of stability constants data using van't Hoff linear plot. Luminescence lifetime measurements and the (X-ray absorption Fine Structure Spectroscopy (EXAFS) were used to reveal information about the hydration number and the coordination modes of these ligands in the complex. In addition, DFT calculation with  $\text{La}^{3+}$  was used to evaluate the effectiveness of the B3LYP/LANL2DZ basis set in structural elucidation of these complexes in solution.

## 2. Experimental

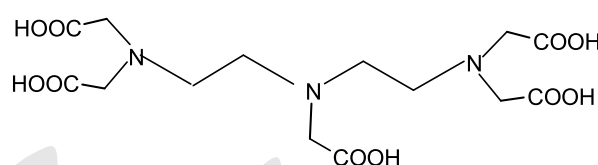
The  $\text{NaClO}_4$  and DTPA were purchased from Aldrich, while  $\text{HClO}_4$ ,  $\text{NaOH}$ , and  $\text{HCl}$ , both solid and standard solutions were obtained from Fisher Scientific. MS-325 and HMDTPA were gifted from Mallinckrodt Medical. The structure of the ligands used in this study is given in Fig. 1. Ligand MS-325 ( $\text{C}_{33}\text{H}_{44}\text{N}_3\text{O}_{14}\cdot\text{H}_2\text{O}$ ) was synthesized as the *R* isomer and is a chemically stable and moderately hygroscopic white powder. To determine if the solid had absorbed additional moisture since the time of elemental analysis, a Karl Fischer titration was performed on the solid immediately prior to use in this study. The new analysis gave a water content of 4.13% which would give  $\text{C}_{33}\text{H}_{44}\text{N}_3\text{O}_{14}\cdot 2.5\text{H}_2\text{O}$  with an effective molecular weight of 783.13. Solutions of the ligands DTPA, MS-325, and HMDTPA were prepared in 0.10 M ( $\text{NaClO}_4$ ) and their concentrations were determined by pH-titration with standard  $\text{NaOH}$ .

Perchlorate stock solutions of  $\text{Ln}_2\text{O}_3$  (except Pm) were prepared by dissolving a known amount of the oxide in a slight excess of perchloric acid (60%, Fisher Scientific) and diluting to a known volume. Their concentrations were determined by complexometric titration with EDTA in the presence of xylenol orange indicator [18]. Di-(2-ethylhexyl) phosphoric acid, (D2EHPA, Sigma-Aldrich) and heptane (Fisher Scientific, ACS) were used as received.

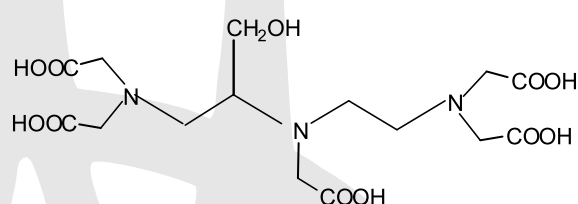
The radioactive tracers  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$  and  $^{152,154}\text{Eu}$  (Oak Ridge National Laboratory) were purified and their purity checked by  $\alpha$ - and/or  $\gamma$ -spectrometry. The working stock of each tracer was prepared in  $\text{HClO}_4$  solution of pH  $\sim 3.0$



1- R(4,4-diphenyl cyclohexyl)-phosphonyl-methyl diethylenetriaminepentaacetic acid (MS-325)



Diethylenetriaminepentaacetic acid (DTPA)



Hydroxymethyldiethylenetriamine pentaacetic acid (HMDTPA)

Fig. 1. Structures of DTPA, MS-325, and HMDTPA used in this study.

such that a 10.0  $\mu\text{L}$  of the solution has a count rate of *ca.* 60 000 cpm. The activities of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ , and  $^{152,154}\text{Eu}$  were measured in a Beckman Liquid Scintillation Counter (LSC) using Ecolite cocktail (ICN, Research Product Division).  $^{248}\text{Cm}$  used for the luminescence studies was purified by passage through a column of Dowex-1 anion exchange resin in 7.5 M  $\text{HNO}_3$ . The collected Cm fraction was evaporated to dryness and re-dissolved in 0.001 M  $\text{HClO}_4$ . The concentration of the  $\text{Cm}^{3+}$  stock solution was determined by  $\alpha$ -spectrometry and liquid scintillation counting.

Accumet 950 (Fisher Scientific) pH meter was used for pH measurements. Solution of pH  $4.00 \pm 0.01$  and  $7.00 \pm 0.01$  buffers were used to calibrate the electrode system. Solutions of bases were standardized by potassium acid phthalate, KHP, titration. Prior to use, KHP was dried at 100 °C for at least 2 h and cooled in the dessicator over silica gel. The electrode was calibrated before each titration by performing titration of a known amount of standardized  $\text{HClO}_4$  with standardized  $\text{NaOH}$  solution at 0.1 M ( $\text{NaClO}_4$ ) as the background electrolyte. A plot of mV (measured) vs. pH (calculated) gave a working slope and intercept so that pH could be read as  $-\log[\text{H}^+]$  directly.

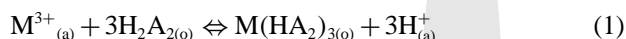
## 2.1 Solvent extraction procedure

The distribution ratio,  $D$ , is defined as the ratio of the total concentrations of the metal ions in an organic and an aqueous phase, and was determined by solvent extraction at 0, 25, 35 and 45 °C. For each extraction experiment, 3.0 mL of the aqueous phase and the organic phase were shaken in a water bath (Cole-Parmer Inst. Co, Polystat Model 1200-00 circulator) at 180 rpm for 1 h at  $\text{pH} = 3.60 \pm 0.05$ . Kinetic measurements indicated that equilibrium was attained in these experiments in about 1 h. The organic solutions (D2EHPA in heptane,  $5 \times 10^{-4}$  for  $\text{Cm}^{3+}$  and  $\text{Am}^{3+}$  and  $2 \times 10^{-4}$  M for  $\text{Eu}^{3+}$ ) were pre-equilibrated with the 0.10 M  $\text{NaClO}_4$  at pH 3.60 prior to use. The aqueous solutions of the reaction mixture were 0.10 M  $\text{NaClO}_4$ , with or without complexing agents. The concentrations of DTPA, MS-325 and HMDTPA were varied in the range of  $1.0 \times 10^{-7}$  to  $6.0 \times 10^{-7}$  M. A 20–30  $\mu\text{L}$  volume of the radioactive tracer solution was added to each vial. After the vials were centrifuged for 3–5 min, 0.50–1.0 mL of duplicate samples was taken from both phases for counting. The remaining aqueous phase was used for measurement of the equilibrium pH.

## 2.2 Data analysis

### M-L system

The extraction of  $\text{M}^{3+}$  ( $\text{M} = \text{Am}$ ,  $\text{Cm}$  and  $\text{Ln}$ ) between the aqueous phase 0.10 M ( $\text{NaClO}_4$ ) and the organic phase (D2EHPA, represented as the dimer  $\text{H}_2\text{A}_2$ ) can be expressed as:



where (a) and (o) represent the aqueous and organic phases, respectively. In the presence of ligand ( $\text{L} = \text{DTPA}$ , MS-325 and HMDTPA) in the aqueous phase, the complexation reaction of the metal ions can be written as:



where  $\beta_{101}$  is the stability constant of the complex formed. The distribution ratio of the trivalent metal ions between the D2EHPA/heptane and the aqueous phase is expressed as:

$$D = [\text{M}^{3+}]_{(\text{o})} / [\text{M}^{3+}]_{(\text{a})} \quad (3)$$

where  $[\text{M}^{3+}]$  represents the total metal ion concentration in the organic and aqueous phases. The polynomial correlating  $D$  values with  $[\text{L}^{5-}]$  and  $\log \beta_{101}$  may be written as:

$$1/D = 1/D_0 \times 1 + \beta_{101} [\text{L}^{5-}] \quad (4)$$

$$D_0/D - 1 = \beta_{101} \times [\text{L}^{5-}] \quad (5)$$

where  $D_0$  is the distribution ratio of metal ions in the absence of ligand.

The pH of the aqueous phase varied slightly after extraction. The measured distribution ratio values,  $D$ , were corrected using the equation:

$$\log D_{\text{corr}} = \log D - n \times (\text{pH} - \text{pH}_{\text{av}}) \quad (6)$$

where  $\text{pH}_{\text{av}}$  is the average pH for each experiment.  $n$  is the experimental slope of the  $\log D_0$  vs. pH plot in the absence

of the ligand. The  $n$  values used for the pH corrections were 2.89–2.78 for  $\text{Am}^{3+}$ , 2.80–2.65 for  $\text{Cm}^{3+}$  and 2.82–2.69 for  $\text{Eu}^{3+}$ . This correction usually did not exceed 5–10% of the  $D$  value for single sample. The error limits for the stability and protonation constants are expressed in terms of 95% confidence limits based upon two or more determinations. To allow comparison in different temperatures, the stability constants values in molarity were converted to values in molality according to equation [19].

$$\log \beta_{\text{m}} = \log \beta_{\text{M}} + \sum_r \nu_r \log \theta \quad (7)$$

where ( $\beta_{\text{M}}$ ) and ( $\beta_{\text{m}}$ ) are the stability constants in molarity and molality, respectively,  $\theta$  is the ratio of the values of molality to molarity for the specific ionic medium and varies for different media and concentrations.  $\sum_r \nu_r$  is the stoichiometric coefficient of the reactions  $\text{M}^{3+} + \text{L}^{5-} \rightleftharpoons \text{M}(\text{L})^{2-}$  ( $\nu_r$  is positive for the products and negative for the reactants), which gives a value of  $\sum_r \nu_r$  of  $-1$  for the complexation reaction.

## 2.3 Potentiometric titrations

Potentiometric titrations were conducted to determine the protonation constants of the ligands and the 1:1 stability constants of  $\text{Ln}^{3+}$  with these ligands using an automated titration system. The titrant solution was delivered by a Metrohm Dosimat 665 motor-driven piston burette. Nitrogen gas was bubbled through the titration solution to remove the dissolved carbon dioxide. The titrations were performed with stirring on a Corning model PC420 stirrer/hot plate. The system was interfaced to a computer that operated software prepared in the laboratory to control burette additions and to record the mV reading of the electrode. The delay between the readings was  $\geq 30$  s to assure equilibrium. After the addition was made, the system waited a mixing time, typically 30 s, before restarting the measurement cycle. Prior to each titration or complexation titration, the electrode was calibrated by an acid-base titration using the standardized perchloric acid and sodium hydroxide solutions at the desired temperatures so that hydrogen ion concentrations could be calculated from the emf readings in the subsequent titrations.

Samples were titrated in 35 mL jacketed cell which was maintained at the desired temperature with the aid of a controlled temperature circulating water bath (Nesslab) under an atmosphere of  $\text{N}_2$ . Titration additions were accomplished using a 25.0 mL digital burette (Metrohm). For the protonation constant measurements, 15.0 mL of 0.001 to 0.0015 M of ligands were titrated with the 0.100 M NaOH over a pH range from 2 to 11, collecting 120 data points per titration. To determine the stability constants of the lanthanide complexes, competition titrations with EDTA were performed at a ratio of  $1\text{Ln}/1\text{L}/2\text{EDTA}$ . For the competition ligand titrations, 1.25 mL of 0.200 M  $\text{Ln}(\text{III})$ , 10 mL of 0.100 M EDTA, 2.5 mL of 2.0 M  $\text{NaClO}_4$  and 8.9 mL of 0.11261 M  $\text{HClO}_4$  were combined in the 50 mL conical flask. 15 mL of this solution was titrated with 0.015 M of ligand solutions ( $\text{L} = \text{DTPA}$ , MS-325 or HMDTPA). The titration data were fitted by HYPERQUAD to calculate the acid dissociation constants and the stability constants. The value of  $\text{p}K_{\text{w}}$  was fixed



at 13.78 for all analyses [20]. The stability constant values of  $\text{Ln}(\text{EDTA})^-$  complex at 0.1 M  $\text{NaClO}_4$  were taken from NIST database [20].

## 2.4 Calorimetry (ITC)

Calorimetric titrations were conducted with an isothermal solution calorimeter system (VP-ITC micro-calorimeter from Micro-Cal Inc. (USA) at 25 °C). The performance of calorimeter was tested by measuring the enthalpy of protonation of 2-bis(2-hydroxyethyl)amino-2-hydroxymethylpropan-1,3-diol. In a typical titration,  $n$  additions of the titrant were made (usually  $n = 40$ ), resulting in  $n$  experimental values of the total heat generated in the titration vessel ( $Q_{\text{ex},j}$ ,  $j = 1$  to  $n$ ). For protonation heat, ligand solution (L) was loaded into the sample cell (1.44 ml), and the acid solution loaded into the injector (240  $\mu\text{l}$ ), which was titrated with approximately 40 aliquots of 6  $\mu\text{l}$   $\text{HClO}_4$  into the cell. The syringe is tailor-made such that the tip acts as a blade-type stirrer to ensure an optimum mixing efficiency at 400 rpm. The heat evolved or absorbed by each injection in the course of titration is directly measured by the ITC unit, producing the raw heat signal, also known as cell feedback (CFB). Integration of each CFB gives the differential enthalpy curve for the titration. The observed heat changes were corrected for the heats of dilution ( $Q_{\text{dil},j}$ ) that were determined in separate runs. For complexation heat, solutions of  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Nd}$ ,  $\text{Eu}$  and  $\text{Dy}$ ) (1.44 mL) were placed in the titration vessel and titrated with L. Multiple titrations with different concentrations of  $\text{Eu}^{3+}$  were performed to reduce the uncertainty. These values were corrected for the heats of dilution of the titrant. The net reaction heat at the  $j$ -th point ( $Q_{r,j}$ ) was obtained from the difference:  $Q_{r,j} = Q_{\text{ex},j} - Q_{\text{dil},j}$ . The set of  $\Delta Q_{r,j}$  data was analyzed with a PC program 'Letagrop' [21] to obtain the enthalpy change for the target reaction. The measurements for each system were repeated at least twice.

## 2.5 Luminescence measurement studies

The  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  lifetime measurement studies were carried out for  $1.0 \times 10^{-4}$  M  $\text{Eu}^{3+}$  and  $2.0\text{--}4.0 \times 10^{-6}$  M  $\text{Cm}^{3+}$  at room temperature in 1.00 cm quartz fluorimeter cells using an instrumental setup similar to that in Ref. [22]. Solutions of the complexes were prepared by mixing the  $\text{Eu}(\text{ClO}_4)_3$  or  $^{248}\text{Cm}$  and the corresponding ligand solutions in 0.10 M ( $\text{NaClO}_4$ ). The pH of the solutions was varied from 3.6–13.0 with dilute  $\text{HClO}_4$  or  $\text{NaOH}$ . The equations  $N_{\text{H}_2\text{O}} = 1.05k_{\text{obs}} - 0.70$ , where  $k_{\text{obs}}$  is the luminescence decay constant in ms [23] were used to calculate the number of water molecules associated with the  $\text{Eu}^{3+}$  complex. For  $\text{Cm}^{3+}$ , the correlation  $N_{\text{H}_2\text{O}} = 0.65k_{\text{obs}} - 0.88$  [5] was used to calculate the number of bound water molecules. An uncertainty of  $\pm 0.5$  is assigned for  $N_{\text{H}_2\text{O}}$  in these measurements [23].

## 2.6 Extended X-ray absorption fine structure (EXAFS)

Three solutions, (1)  $\text{Eu}:\text{DTPA}$  1:2 pH = 9.0, (2)  $\text{Eu}:\text{MS-325}$ , 1:2, pH  $\sim$  9.0 (3)  $\text{Eu}:\text{HMDTPA}$ , 1:2, pH  $\sim$  9.0 were used for the EXAFS experiments. The concentration of  $[\text{Eu}^{3+}]$  was  $\sim 0.015$  M in all solutions. The analysis was

performed at the  $\text{Eu } L_{\text{III}}$  absorption edge (6.977 keV) to determine the association of  $\text{Eu}^{3+}$  with the complexants DTPA, MS-325 and HMDTPA. The aqueous samples (1.0 ml) were placed in heat sealed polypropylene bags and mounted on an Al sample holder having geometry of 2 mm (H)  $\times$  20 mm (L) with a 1.5 mm thickness. Fluorescence data were collected using a 13 element Ge detector on beam-line  $\times 10\text{C}$  at the National Synchrotron Light Source (NSLS) (Brookhaven National Laboratory). The absorption edge energy was calibrated using the first inflection point of the spectrum of an Fe foil (7.112 keV). The EXAFS data were processed using the program Ifeffit [24]. The theoretical EXAFS modeling code FEFF6 was used to calculate the back-scattering phase and amplitude information for individual neighboring atoms [25]. The phase and amplitude functions were determined using the crystal structure for europium terephthalate [26]. Four scans were collected per sample and the data were averaged. The amplitude reduction factor ( $S_0^0$ ) was fixed at 1.0 for all of the fits. Fitting data for the samples were obtained by comparison with the standards.

## 3. Results and discussion

### 3.1 Complexation thermodynamics

The protonation and the thermodynamics of stepwise protonation of L ( $\text{L} = \text{DTPA}$ , MS-325 and HMDTPA) are summarized in Tables 1 and 2. The ligands MS-325 and HMDTPA, behave similarly to DTPA in term of protonation constants. However, the first two protonation constants are significantly depressed for MS-325, while for HMDTPA the first protonation constant shows a slight increased in comparison to DTPA. This could be either an electron withdrawing effect of the phosphodiester moiety or an enhanced binding of sodium ion in MS-325. The protonation constant values determined in the present investigation agree with the values reported in the literature for the DTPA. There is only one reported work by Choppin *et al.*, [27] in which protonation constants of MS-235 as well as their complexation constants with  $\text{Gd}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were measured and to the best of our knowledge there is no reported protonation constants value for HMDTPA in the literature. The protonation constants of all three ligands decreased significantly as the temperature was increased (except log  $K_4$  value for HMDTPA, Table 1), suggesting that the protonation of these ligands are weakened at higher temperatures.

The enthalpy of protonation of these ligands measured by microcalorimetry are shown in Table 2. For DTPA, the enthalpies of protonation determined directly by microcalorimetry are all negative, consistent with the general trends that all protonation constants decrease as the temperature is increased. The large negative enthalpies of protonation suggest that the first two protonation steps probably occur on the nitrogen atoms and zwitterions similar to those reported for EDTA [19] form in the protonated DTPA species. For MS-325 and HMDTPA, the first three protonation steps ( $\text{HL}^{4-}$ ,  $\text{H}_2\text{L}^{3-}$  and  $\text{H}_3\text{L}^{2-}$ ) are negative, while the last two protonation steps ( $\text{H}_4\text{L}^-$ ,  $\text{H}_5\text{L}$ ) are either positive or slightly negative (Table 2).

Fig. 2 shows speciation diagrams for the  $\text{Am}^{3+}$  with three ligands studied. The protonated complex was not ob-

**Table 1.** Protonation constants of DTPA, MS-325 and HMDTPA at  $I = 0.10$  M ( $\text{NaClO}_4$ );  $T = 0$ – $45$  °C ( $\text{H}_{n-1}\text{L} + \text{H} \rightleftharpoons \text{H}_n\text{L}$ ;  $n = 1$ – $5$ ).

Ligands	Temp. (°C)	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$
DTPA	0	$10.27 \pm 0.05$	$8.95 \pm 0.05$	$5.06 \pm 0.06$	$3.22 \pm 0.10$	$2.18 \pm 0.08$
	25	$10.17 \pm 0.03$	$8.75 \pm 0.02$	$4.52 \pm 0.04$	$2.84 \pm 0.03$	$2.12 \pm 0.07$
	25 <sup>a</sup>	10.42	8.76	4.42	2.56	1.79
	25 <sup>b</sup>	10.49	8.60	4.28	2.64	2.00
	20 <sup>c</sup>	10.55	8.60	4.26	2.41	2.08
	35	$9.80 \pm 0.05$	$8.63 \pm 0.04$	$4.44 \pm 0.06$	$2.79 \pm 0.08$	$2.07 \pm 0.06$
	45	$9.83 \pm 0.05$	$8.42 \pm 0.04$	$4.23 \pm 0.08$	$2.78 \pm 0.08$	$2.04 \pm 0.05$
MS-325	0	$10.02 \pm 0.05$	$8.92 \pm 0.04$	$4.72 \pm 0.05$	$3.03 \pm 0.05$	$2.62 \pm 0.08$
	25	$9.64 \pm 0.05$	$8.57 \pm 0.05$	$4.46 \pm 0.06$	$2.87 \pm 0.13$	$2.41 \pm 0.12$
	25 <sup>d</sup>	$9.56 \pm 0.09$	$8.31 \pm 0.09$	$4.41 \pm 0.09$	$2.92 \pm 0.03$	$2.43 \pm 0.15$
	35	$9.60 \pm 0.04$	$8.46 \pm 0.02$	$4.57 \pm 0.03$	$2.82 \pm 0.03$	$2.19 \pm 0.05$
	45	$9.58 \pm 0.03$	$8.38 \pm 0.02$	$4.51 \pm 0.01$	$2.76 \pm 0.02$	$2.14 \pm 0.02$
HMDTPA	0	$10.83 \pm 0.06$	$8.52 \pm 0.07$	$4.98 \pm 0.04$	$2.84 \pm 0.11$	$2.21 \pm 0.10$
	25	$10.71 \pm 0.07$	$8.47 \pm 0.07$	$4.64 \pm 0.09$	$2.82 \pm 0.12$	$2.22 \pm 0.11$
	35	$10.11 \pm 0.08$	$8.42 \pm 0.04$	$4.40 \pm 0.05$	$2.81 \pm 0.09$	$2.24 \pm 0.07$
	45	$9.80 \pm 0.05$	$8.38 \pm 0.06$	$4.35 \pm 0.09$	$2.85 \pm 0.11$	$2.07 \pm 0.10$

a: 0.1 M  $\text{KNO}_3$  from Ref. [20b];b: 0.1 M  $\text{KCl}$  from Ref. [44];

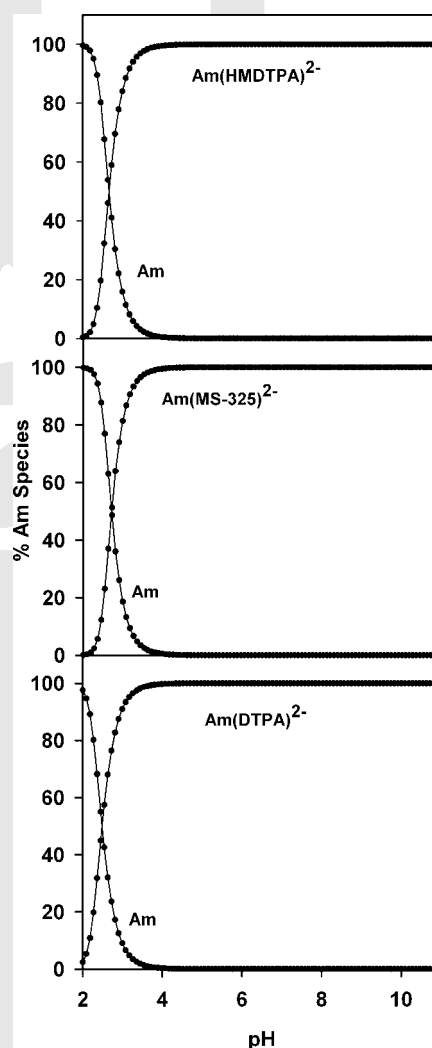
c: 0.1 M from Ref. [20b]; and

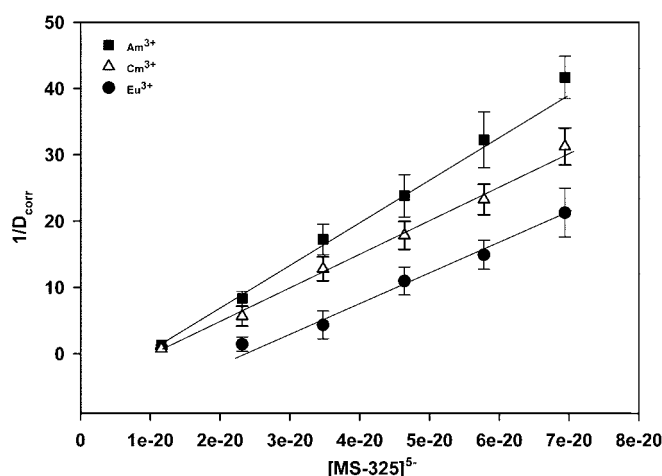
d: from Ref. [27].

**Table 2.** Thermodynamic data for stepwise protonation of L at 25 °C;  $I = 0.10$  M ( $\text{NaClO}_4$ ).

Ligands	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
DTPA( $\text{H}_5\text{L}$ )			
$\text{H} + \text{L} = \text{HL}$	$-58.03 \pm 0.17$	$-35.15 \pm 2.56$	$77 \pm 9$
$\text{HL} + \text{L} = \text{H}_2\text{L}$	$-49.93 \pm 0.11$	$-13.09 \pm 0.58$	$123 \pm 2$
$\text{H}_2\text{L} + \text{L} = \text{H}_3\text{L}$	$-25.79 \pm 0.23$	$-4.21 \pm 0.06$	$72 \pm 1$
$\text{H}_3\text{L} + \text{L} = \text{H}_4\text{L}$	$-16.20 \pm 0.17$	$-0.80 \pm 0.13$	$52 \pm 1$
$\text{H}_4\text{L} + \text{L} = \text{H}_5\text{L}$	$-12.1 \pm 0.40$	$-0.70 \pm 0.32$	$38 \pm 2$
MS-325( $\text{H}_5\text{L}$ )			
$\text{H} + \text{L} = \text{HL}$	$-55.00 \pm 0.29$	$-26.62 \pm 1.34$	$95 \pm 5$
$\text{HL} + \text{L} = \text{H}_2\text{L}$	$-48.90 \pm 0.17$	$-10.06 \pm 0.41$	$130 \pm 2$
$\text{H}_2\text{L} + \text{L} = \text{H}_3\text{L}$	$-26.93 \pm 0.34$	$-1.51 \pm 0.09$	$85 \pm 2$
$\text{H}_3\text{L} + \text{L} = \text{H}_4\text{L}$	$-16.38 \pm 0.74$	$-0.48 \pm 0.04$	$53 \pm 2$
$\text{H}_4\text{L} + \text{L} = \text{H}_5\text{L}$	$-13.75 \pm 0.68$	$3.21 \pm 0.70$	$57 \pm 3$
HMDTPA( $\text{H}_5\text{L}$ )			
$\text{H} + \text{L} = \text{HL}$	$-61.10 \pm 0.40$	$-35.8 \pm 3.99$	$85 \pm 13$
$\text{HL} + \text{L} = \text{H}_2\text{L}$	$-48.33 \pm 0.40$	$-12.53 \pm 1.34$	$120 \pm 5$
$\text{H}_2\text{L} + \text{L} = \text{H}_3\text{L}$	$-26.48 \pm 0.51$	$-4.02 \pm 0.76$	$75 \pm 3$
$\text{H}_3\text{L} + \text{L} = \text{H}_4\text{L}$	$-16.09 \pm 0.68$	$2.11 \pm 1.3$	$61 \pm 5$
$\text{H}_4\text{L} + \text{L} = \text{H}_5\text{L}$	$-12.67 \pm 0.63$	$1.20 \pm 0.06$	$46 \pm 2$

served under the conditions employed in this study, but has been reported for  $\text{GdH}(\text{DTPA})^-$ ,  $\text{EuH}(\text{DTPA})^-$  and  $\text{NdH}(\text{DTPA})^-$  [27, 28]. Linear curves of  $1/D_{\text{corr}}$  vs.  $[\text{L}]^{5-}$  for  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Eu}^{3+}$  (Fig. 3, representative graph for  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Eu}^{3+}$  for MS-325 at 25 °C) indicate the formation of only 1 : 1 complexes. The stability constants of the  $\text{Ln}^{3+}$  with these ligands determined by competition titrations are summarized in Table 3, while those with  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Eu}^{3+}$  at different temperatures measured by solvent extraction are listed in Table 4. Representative potentiometric titration curves for the formation of  $\text{Gd}$ -DTPA,  $\text{Yb}$ -MS-325 and  $\text{Lu}$ -MS-325 are shown in Fig. 4. The best fit of the data by the Hyperquad program indicates that only monomeric

**Fig. 2.** Speciation diagrams for  $\text{Am}^{3+}$  with DTPA, MS-325 and HMDTPA, drawn at  $[\text{M}] = [\text{L}] = 1$  mM.



**Fig. 3.** The variation of  $1/D_{\text{corr}}$  for  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Eu}^{3+}$  as a function of  $[\text{MS-325}]^{5-}$ ;  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ) and  $T = 25^\circ\text{C}$ ;  $[\text{D2EHPA}] = 5.0 \times 10^{-4} \text{ M}$  for  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  and  $2.0 \times 10^{-4} \text{ M}$  for  $\text{Eu}^{3+}$ .

complex, ML form during the titration. For comparison purpose, the literature stability constants values for these ligand are also included in Table 4. The values at 0.1 M from this work Am-DTPA (22.57), Cm-DTPA (22.64), and Eu-DTPA (22.56) are in fair agreement with the values of Am-DTPA (22.92), Cm-DTPA (22.99) and Eu-DTPA (22.40) reported by Baybarz at 0.1 M  $\text{NH}_4\text{ClO}_4$  [14]. However, our value of Gd-MS-325 = 22.63 is slightly higher than the value measured by Choppin *et al.*, for Gd-MS-325 = 22.11 at the same ionic strength [27]. The stability constants values for other members of the lanthanide series are not reported, while for actinides no such values are available in the literature.

The stability constant values of our three ligands vary non-monotonically across the Ln-series. Fig. 5 shows the plot of free energy of complexation ( $\Delta G$ ) vs. lanthanide ionic radius for the MS-325 and HMDTPA complexes (values of ionic radii were taken from Ref. [29] for CN = 9). The  $\Delta G$  gradually increases from La to Sm, weakly de-

**Table 3.** Stability constants of  $\text{Ln}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  with DTPA, MS-325 and HMDTPA at  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ );  $T = 25^\circ\text{C}$  for the reaction ( $\text{M}^{3+} + \text{L}^{5-} = \text{ML}^{2-}$ ).

$\text{M}^{3+}$	DTPA	MS-325	HMDTPA	Method
La	$19.36 \pm 0.06$	$18.97 \pm 0.06$	$19.42 \pm 0.08$	pot
Pr	$21.22 \pm 0.09$	$19.62 \pm 0.07$	$21.26 \pm 0.07$	pot
Nd	$21.45 \pm 0.08$	$20.41 \pm 0.11$	$21.46 \pm 0.09$	pot
Sm	$21.58 \pm 0.07$	$20.85 \pm 0.10$	$21.48 \pm 0.08$	pot
Eu	$22.49 \pm 0.11$	$21.58 \pm 0.09$	$22.58 \pm 0.09$	pot
Gd	$22.63 \pm 0.08$	$21.82 \pm 0.07$	$22.70 \pm 0.12$	pot
Tb	$22.72 \pm 0.09$	$22.02 \pm 0.12$	$22.78 \pm 0.08$	pot
Dy	$22.79 \pm 0.10$	$22.15 \pm 0.12$	$22.81 \pm 0.11$	pot
Ho	$22.75 \pm 0.10$	$22.18 \pm 0.08$	$22.76 \pm 0.12$	pot
Er	$22.73 \pm 0.10$	$22.10 \pm 0.12$	$22.74 \pm 0.11$	pot
Tm	$22.72 \pm 0.10$	$22.12 \pm 0.10$	$22.75 \pm 0.12$	pot
Yb	$22.61 \pm 0.11$	$22.09 \pm 0.09$	$22.69 \pm 0.09$	pot
Lu	$22.53 \pm 0.06$	$21.78 \pm 0.09$	$22.54 \pm 0.07$	pot
Am	$22.57 \pm 0.14$	$21.65 \pm 0.13$	$22.63 \pm 0.14$	sx
Cm	$22.64 \pm 0.13$	$21.77 \pm 0.15$	$22.60 \pm 0.15$	sx
Eu	$22.56 \pm 0.14$	$21.65 \pm 0.13$	$22.58 \pm 0.16$	sx

pot = potentiometric, sx = solvent extraction.

The uncertainties listed are the standard errors provided by the statistics of the non-linear regression analysis of individual data sets as carried out by the HYPERQUAD program.

creases between Eu and Gd, and then slowly increases for Tb and Dy, and finally decreases from Er to Lu. Such stability trend is often observed in Ln-aminopolycarboxylate complexes, if the number of donor atoms is seven or more [30]. For instance, the stability constant values increase monotonically across the Ln-series for the ligands with fewer coordination sites (*e.g.*, EDTA, CDTA (trans-1,2 diaminocyclohexanetetraacetic acid) and TMEDTA (1, 4 dinitrobutane tetraacetic acid)) [31], while stability trend similar to those observed in this study were reported for the heptadentate Ln-TEDTA (thiobis(ethylenediamine tetraacetic acid)), Ln-DEATA (*N,N*-bis (2-aminoethyl)aniline tetraacetic acid (BEATA)) [30], and octadentate Ln-DTPA-MA (DTPA-*N*-

**Table 4.** Stability constants of  $\text{Eu}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  with DTPA, MS-325 and HMDTPA at  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ );  $T = 0-45^\circ\text{C}$ .

	0	25	35	45	Ref.
$\text{Eu}^{3+} + \text{DTPA}^{5-} = \text{Eu}(\text{DTPA})^{2-}$	$22.97 \pm 0.14$	$22.56 \pm 0.14$ $22.40 \pm 0.07^a$ $22.39 \pm 0.08^b$ $20.87 \pm 0.07^c$ $22.77 \pm 0.04$ $21.00 \pm 0.08^d$ $20.97 \pm 0.19^d$	$22.31 \pm 0.15$	$22.11 \pm 0.16$	This work [14] [15] [45] [46] [28] [28]
$\text{Am}^{3+} + \text{DTPA}^{5-} = \text{Am}(\text{DTPA})^{2-}$	$22.98 \pm 0.15$	$22.57 \pm 0.14$ $22.92 \pm 0.02^a$ $21.14^c$	$22.30 \pm 0.15$	$22.02 \pm 0.14$	This work [14] [17]
$\text{Cm}^{3+} + \text{DTPA}^{5-} = \text{Cm}(\text{DTPA})^{2-}$	$23.01 \pm 0.15$	$22.64 \pm 0.13$ $22.99 \pm 0.01^a$ $21.26^c$	$22.31 \pm 0.16$	$22.04 \pm 0.14$	This work [14] [17]
$\text{Eu}^{3+} + \text{MS-325} = \text{Eu}(\text{MS-325})^{2-}$	$21.99 \pm 0.16$	$21.65 \pm 0.13$	$21.58 \pm 0.15$	$21.40 \pm 0.16$	This work
$\text{Am}^{3+} + \text{MS-325} = \text{Am}(\text{MS-325})^{2-}$	$22.04 \pm 0.16$	$21.77 \pm 0.13$	$21.56 \pm 0.14$	$21.46 \pm 0.15$	This work
$\text{Cm}^{3+} + \text{MS-325} = \text{Cm}(\text{MS-325})^{2-}$	$22.02 \pm 0.14$	$21.65 \pm 0.15$	$21.56 \pm 0.16$	$21.41 \pm 0.16$	This work
$\text{Eu}^{3+} + \text{HMDTPA} = \text{Eu}(\text{HMDTPA})^{2-}$	$23.01 \pm 0.15$	$22.58 \pm 0.13$	$22.18 \pm 0.16$	$21.86 \pm 0.15$	This work
$\text{Am}^{3+} + \text{HMDTPA} = \text{Am}(\text{HMDTPA})^{2-}$	$23.09 \pm 0.17$	$22.63 \pm 0.15$	$22.32 \pm 0.14$	$22.01 \pm 0.15$	This work
$\text{Cm}^{3+} + \text{HMDTPA} = \text{Cm}(\text{HMDTPA})^{2-}$	$23.05 \pm 0.16$	$22.60 \pm 0.14$	$22.32 \pm 0.15$	$21.95 \pm 0.15$	This work

a: 0.1  $\text{NH}_4\text{ClO}_4$ ; b: 0.1  $\text{KNO}_3$ ; c: 0.5  $\text{NaClO}_4$ ; d: 1.0 M  $\text{NaClO}_4$ .



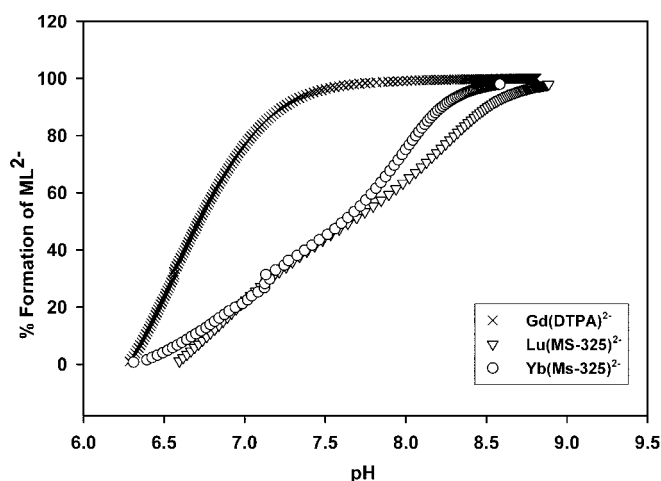


Fig. 4. Potentiometric titration curve for the formation of Gd-DTPA, Lu-MS-325 and Yb-MS-325 complexes,  $I = 0.1$  M NaClO<sub>4</sub>.  $[M^{3+}] = 0.005$  M,  $[L] = 0.015$  M,  $[EDTA] = 0.04$  M.

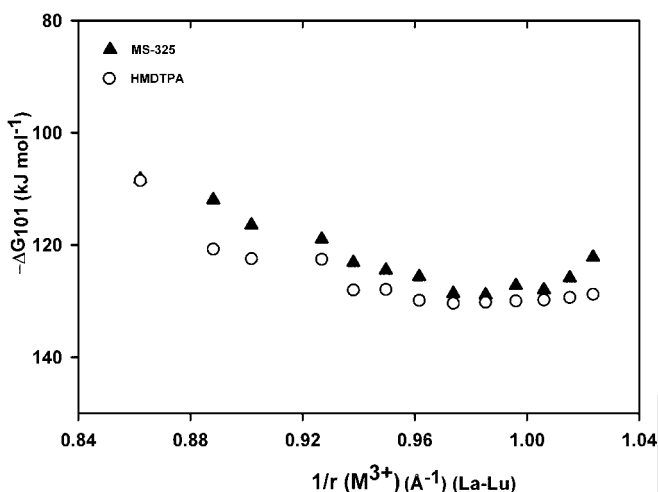


Fig. 5. Variation of stability constant of Ln-HMDTPA and Ln-MS-325 complexes with ionic radii along the lanthanide series. Ionic radius corresponds to a CN = 9.

mono methylamide) complexes [32]. This is either because of the change in hydration number from 9 to 8 with decreasing ionic radii or the steric hindrance imposed by various donor groups upon complexation. A comparison of the stability constants of the complexes demonstrates the order: DTPA  $\approx$  HMDTPA  $>$  MS-325, indicating that introduction of phosphodiester groups on the ethylenediamine backbone of DTPA decreases the stability constant of the  $M(\text{MS-325})^{2-}$  complex. On the other hand, the similarity in the stability constant values of HMDTPA and DTPA with these cations implies that the incorporation of hydroxymethyl groups has not significantly altered the nature and the strength of the complexation. This may be explained by the steric effect of the bulky substituents constraining the ligands into a chelation in the MS-325 complex.

Fig. 6 shows the stability constant plot of some Gd-complexes with several closely related DTPA ligands. All these ligands are, like the parent ligand DTPA, octadentate. An increase in the steric constraints of the polyaminocarboxylate ligand either by increasing the number of groups in the ligand backbone or by increasing

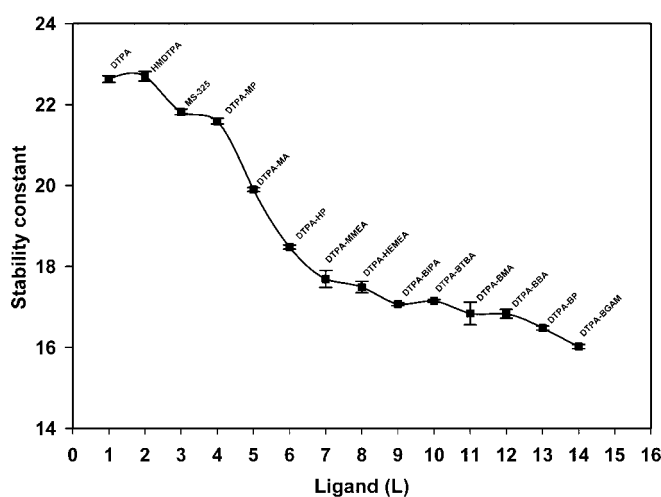
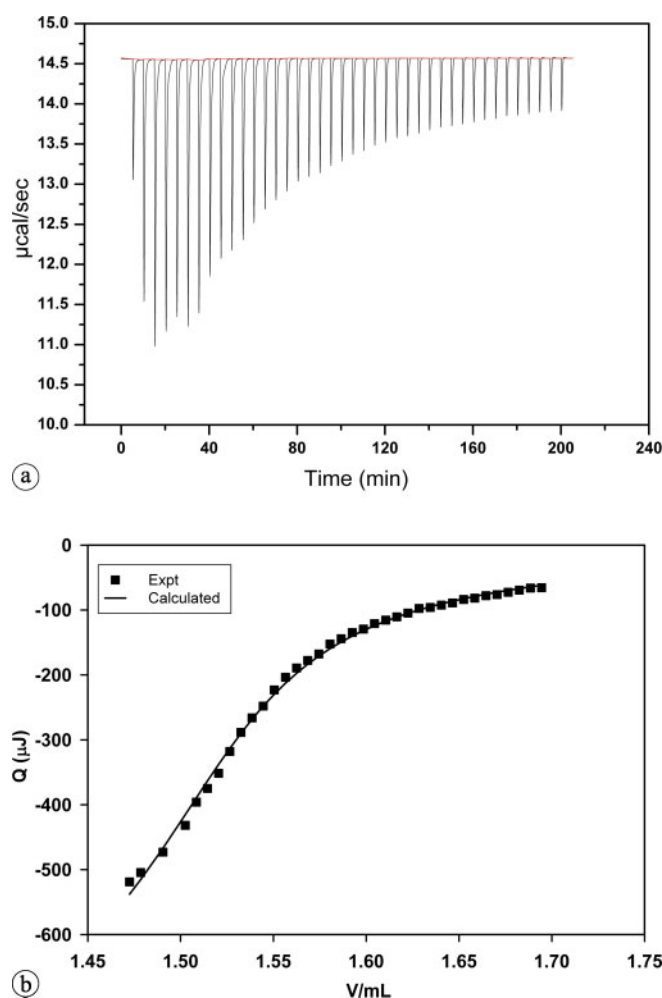


Fig. 6. Variation of the stability constant,  $\log \beta_{101}$ , of some Gd complexes with DTPA derivatives ligands.

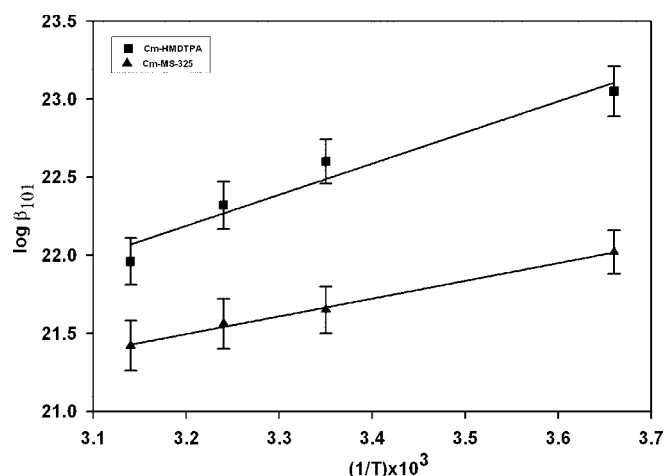
the number of groups in the carboxylate arms decrease the stability values by *ca.* three to six log units. For example, DTPA-BMA (DTPA-bis(methoxyethylamide)),  $\text{Gd}(\text{DTPA-BMA}) = 16.84 \pm 0.28$  [33], DTPA-MMEA (DTPA-bis(methylmethoxyethylamide)),  $\text{Gd}(\text{DTPA-MMEA}) = 17.69 \pm 0.21$  [32], DTPA-HEMEA (DTPA-bis(hydroxyethylmethoxyethylamide)),  $\text{Gd}(\text{DTPA-HEMEA}) = 17.49 \pm 0.14$  [33], DTPA-BIPA (DTPA-bis(iso-propylamide)),  $\text{Gd}(\text{DTPA-BIPA}) = 17.07 \pm 0.04$  [34], DTPA-BTBA (DTPA-bis(tert-butylamide)),  $\text{Gd}(\text{DTPA-BTBA}) = 17.15 \pm 0.03$  [34], DTPA-BBA (DTPA-bis(benzylamide)),  $\text{Gd}(\text{DTPA-BBA}) = 16.48 \pm 0.05$  [34], in all these cases two of the terminal carboxylate groups of DTPA are replaced by amide functionalities result in complexes with lower stability than DTPA. This is because of weaker donor ability of the amide group and the lower basicity of the terminal nitrogen atoms. Similar decrease in stability is also reported for DTPA-BGAM ( $\log \beta_{\text{Gd-DTPA-BGAM}} = 16.02 \pm 0.05$ ) [35] and DTPA-BP ( $(N,N')$ -bis(2-pyridylmethyl-diethylenetriaminetriaacetic acid)) ( $\log \beta_{\text{Gd-DTPA-BP}} = 16.83 \pm 0.11$ ,  $I = 0.1$  M NaCl) [36] in which two terminal carboxylate groups of DTPA are replaced by sugar and pyridylmethyl groups, respectively. The decrease in stability is not only restricted to terminally substituted DTPA ligands. The middle substituted DTPA ligands *i.e.*, DTPA-MA (DTPA-monoamide), DTPA-MP ( $N'$ -2-pyridylmethyl-diethylenetriaminetetraacetic acid) and DTPA-HP ( $N$ -2-hydroxypropyl-diethylenetriaminetetraacetic acid) in which a middle carboxylate group of DTPA is replaced by amide, pyridylmethyl or hydroxylpropyl groups, respectively are also reported to form weaker complexes than DTPA ( $\log \beta_{\text{Gd-DTPA-MA}} = 19.9 \pm 0.048$  at  $I = 0.1$  M KCl [32],  $\log \beta_{\text{Gd-DTPA-MP}} = 21.59 \pm 0.07$  [36], and  $\log \beta_{\text{Gd-DTPA-HP}} = 18.48 \pm 0.05$  [36] at  $I = 0.1$  M Me<sub>4</sub>NNO<sub>3</sub>). However, these modifications of the DTPA ligands do not significantly affect the coordination geometry about the central metal cations.

Fig. 7 shows representative calorimetric titration curve of the three successive protonation steps of DTPA ( $\text{H}_3\text{L}^{2-}$ ,  $\text{H}_4\text{L}^-$ ,  $\text{H}_5\text{L}$ ). Using the data from multiple titrations with different reagent concentrations in conjunction with the stability constants obtained by potentiometer and extraction experiments, the enthalpies of complexation at 25 °C were



**Fig. 7.** Calorimetric titrations of protonation of DTPA,  $t = 25^\circ\text{C}$ ,  $I = 0.1\text{ M NaClO}_4$ .  $V_0 = 1.45\text{ mL}$ ; titrant:  $0.028\text{ M HClO}_4$  in  $0.1\text{ M NaClO}_4$ . Initial concentrations of DTPA =  $0.0024\text{--}0.0055\text{ M}$  DTPA. The upper figure is the thermogram of the titrations.

calculated. The enthalpy values as well as the entropies of complexation calculated are summarized in Table 5. The stability constants of Cm-HMDTPA and Cm-MS-325 obtained at different temperatures are plotted as functions of  $1/T$  (K) are shown in Fig. 8. The linear correlations between  $\log \beta$  and  $1/T$  suggest that the effect of temperature on the complexation could be approximately described with the constant enthalpy approach in the temperature range of  $0\text{--}45^\circ\text{C}$ . From the slopes of the linear fits, the enthalpies of complexation (in  $\text{kJ mol}^{-1}$ ) for reaction 2 were calculated (Table 5). Our enthalpy value of  $-32.6 \pm 1.1\text{ kJ mol}^{-1}$  agrees well with the value selected in the NIST database for the Eu-DTPA complex ( $-32\text{ kJ mol}^{-1}$  at  $0.1\text{ M}$ ). For Am and Cm, no such values were recommended in the NIST database. The complexation enthalpies are negative as expected for strong metal-ligand interaction, whereas the entropy values are positive which is consistent with inner sphere coordination with displacement of water molecules from the hydration sphere of the metal cations. This is common for chelating ligands [29], and is observed in this work. The complexation enthalpies ( $\Delta H$ ) for M-DTPA and M-HMDTPA complexation are *ca.*  $15\text{ kJ mol}^{-1}$  more exothermic than the corresponding complexes with MS-325. The M–N interaction strongly influences the value of  $\Delta H$  and



**Fig. 8.** Van't Hoff plot of the stability constants of Cm-HMDTPA and Cm-MS-325 complexes,  $I = 0.1\text{ M NaClO}_4$ .

the large exothermicity of the Eu-DTPA and Eu-HMDTPA complexation suggests that M–N interactions are stronger as compared to the M–N interactions in M-MS-325. The large positive entropies values are responsible for the higher stabilities of these ligands with *f*-element cations.

### 3.2 Luminescence lifetime measurements

Table 6 lists the luminescence lifetimes and the calculated  $N_{\text{H}_2\text{O}}$  values for the  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  complexes with L in  $0.10\text{ M (NaClO}_4)$ . The aqueous  $\text{Eu}^{3+}$  shows peak at  $578.90\text{ nm}$  with lifetime of  $113 \pm 5$  and  $N_{\text{H}_2\text{O}}$  of  $8.5$ , while for  $\text{Cm}^{3+}$  the position of the peak is at  $396.70\text{ nm}$  with lifetime of  $64 \pm 3$  and  $N_{\text{H}_2\text{O}}$  of  $9.1$ . The fluorescence lifetime of  $\text{Cm}^{3+}$  in solution was first observed by Beitz and Hessler in 1980 [37]. Since then several groups have reported the lifetime for the  $593\text{ nm}$  emission of  $\text{Cm}^{3+}$ . As shown in Table 6, the lifetimes at room temperature in pure  $\text{H}_2\text{O}$  measured by different groups agree well with each other ( $65\text{--}68\text{ }\mu\text{s}$  for  $\text{Cm}^{3+}$ ).

The excitation spectra of Eu-L at a ratio of  $1:2$  and  $\text{pH} = 3.6$  show a peak at  $579.91\text{ nm}$  with lifetimes and  $N_{\text{H}_2\text{O}}$  (Table 6 and Fig. 9) consistent with the formation of  $\text{Eu(L)(H}_2\text{O)}^{2-}$ . Lack of change in  $N_{\text{H}_2\text{O}}$  values up to  $\text{pH } 13.0$  indicates the formation of  $1:1$  complex over this pH range. Brittain *et al.*, [38] also reported no change in the hydration number for  $\text{Eu(DTPA)}^{2-}$  up to  $\text{pH}$  of about  $11.0$ . The lifetime value measured in various studies for the  $\text{Eu(DTPA)}^{2-}$  species agrees with each other (Table 6). The formation of hydrolyzed species,  $\text{Eu(L)(OH)}^{3-}$  as reported in the case of  $\text{Eu(DTPA-Dien)(OH)}^-$  (DTPA-Dien =  $1,4,7\text{-tris(carboxymethyl)-9,17-dioxo-1,4,7,10,13,16-hexa-azocycloocta decane}$ ) and  $\text{Eu(EDTA)(OH)(H}_2\text{O)}_2^{2-}$  was not observed in our study. The crystal structure of  $\text{Eu(DTPA)}^{2-}$  has been shown to be an octadentate in which DTPA binds *via* five carboxylate oxygen atoms and three amine nitrogen atoms with one water of hydration remain attached to the  $\text{Eu}^{3+}$  [39].

The  $\text{Cm}^{3+}$  also forms  $1:1$  complex over pH range  $3.6\text{--}13.0$ . However,  $\text{Cm(L)}^{2-}$  has a slightly larger hydration number ( $N_{\text{H}_2\text{O}} = 1.5$ ) than that of  $\text{Eu(L)}^{2-}$ . This can be attributed to the larger total average coordination number for  $\text{Cm}^{3+}$  ( $9.0 \pm 0.5$ ) as compared to that the  $\text{Eu}^{3+}$  ( $8.5 \pm 0.5$ )



**Table 5.** Thermodynamic data of the 1 : 1 complexes of Ln, Am and Cm with DTPA, MS-325 and HMDTPA at  $I = 0.1$  M ( $\text{NaClO}_4$ );  $T = 25$  °C.

	Method	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	Ref.
<b>DTPA</b>					
Nd	c	$-122.39 \pm 0.46$	$-29.7 \pm 1.3$	$311 \pm 5$	This work
Eu	c	$-128.32 \pm 0.63$	$-32.6 \pm 1.1$	$295 \pm 4$	This work
	sx	$-128.72 \pm 0.79$	$-30.8 \pm 7.3$	$328 \pm 25$	This work
	c	$-127.75 \pm 0.4$	$-32$	$320$	[20a]
	c	$-119.1 \pm 0.4^a$	$-39.8 \pm 1.5$	$266 \pm 5$	[45]
Dy	c	$-130.00 \pm 0.57$	$-33.1 \pm 1.5$	$325 \pm 5$	This work
Am	sx	$-128.78 \pm 0.79$	$-34.1 \pm 7.2$	$317 \pm 24$	This work
	c	$-120.60 \pm 0.6^a$	$-39.5 \pm 1.0$	$272 \pm 5$	[45]
Cm	sx	$-129.18 \pm 0.74$	$-34.7 \pm 7.2$	$317 \pm 24$	This work
<b>MS-325</b>					
Nd	c	$-116.46 \pm 0.63$	$-16.8 \pm 2.1$	$334 \pm 7$	This work
Eu	c	$-123.53 \pm 0.51$	$-18.9 \pm 1.2$	$351 \pm 4$	This work
Eu	sx	$-123.13 \pm 0.74$	$-20.7 \pm 7.7$	$343 \pm 26$	This work
Dy	c	$-126.38 \pm 0.68$	$-20.2 \pm 2.8$	$356 \pm 10$	This work
Am	sx	$-124.22 \pm 0.74$	$-21.6 \pm 7.6$	$344 \pm 20$	This work
Cm	sx	$-123.53 \pm 0.86$	$-22.0 \pm 7.3$	$341 \pm 25$	This work
<b>HMDTPA</b>					
Nd	c	$-122.45 \pm 0.51$	$-39.7 \pm 2.5$	$278 \pm 9$	This work
Eu	c	$-128.27 \pm 0.51$	$-41.9 \pm 2.2$	$289 \pm 8$	This work
Eu	sx	$-128.84 \pm 0.91$	$-41.2 \pm 7.4$	$294 \pm 25$	This work
Dy	sx	$-130.38 \pm 0.62$	$-43.6 \pm 2.7$	$291 \pm 9$	This work
Am	sx	$-129.12 \pm 0.79$	$-39.4 \pm 8.0$	$301 \pm 22$	This work
Cm	sx	$-128.95 \pm 0.85$	$-38.9 \pm 7.7$	$302 \pm 26$	This work

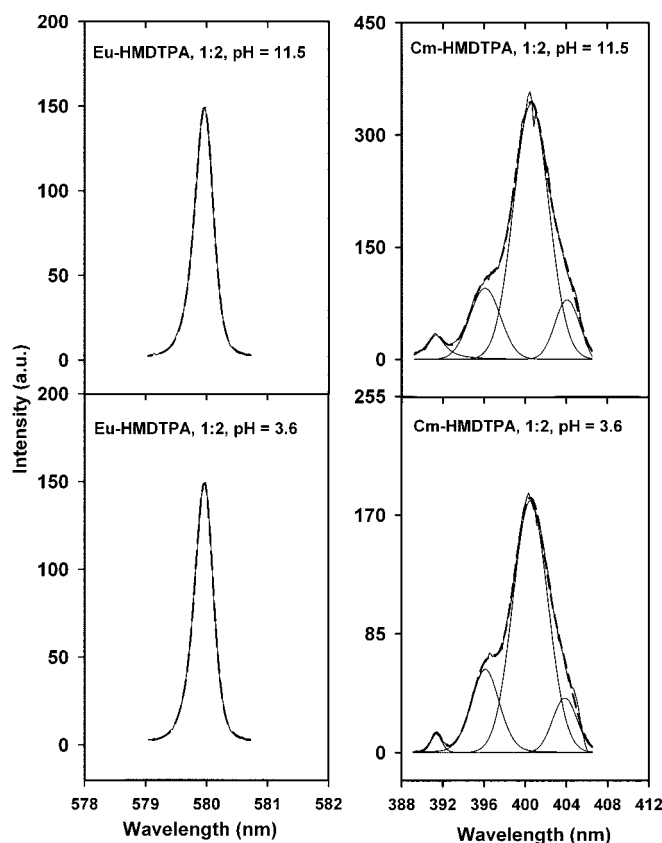
a: 0.5 M ( $\text{NaClO}_4$ ); pw = present work; sx = solvent extraction; c = calorimeter.

**Table 6.** Luminescence lifetime and calculated number of primary coordination sphere water for  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  complexes with L ( $I = 0.10$  M  $\text{NaClO}_4$ );  $T = 25$  °C.

Components	pH/medium	Peak positions (nm)	Species	Lifetime ( $\mu\text{s}$ )	$N_{\text{H}_2\text{O}}$ ( $\pm 0.5$ )	Ref.
$\text{Eu}^{3+}$ (aq)	2.2	578.90	—	$113 \pm 5$	8.5	This work
	2.0	579.04	—	117	9.0	[47]
$\text{Cm}^{3+}$ (aq)	2.5	396.7	—	$64 \pm 3$	9.1	This work
		397	—	—	9.2	[5]
	0.1 M $\text{HClO}_4$	593	—	$68 \pm 3$	8.7	[48]
	1 M $\text{HClO}_4$	593.8	—	63	9.4	[48]
	0.1 M $\text{HClO}_4$ / 1 M HCl	593	—	$65 \pm 2$	9.1	[48]
Eu-DTPA	3.6–11.0	579.91	$\text{Eu}(\text{DTPA})^{2-}$	$650 \pm 4$	0.9	This work
	13.0	579.98	$\text{Eu}(\text{DTPA})^{2-}$	$549 \pm 5$	1.2	This work
	2.0–11.0	—	$\text{Eu}(\text{DTPA})^{2-}$	680	0.95	[5]
	—	579.84	$\text{Eu}(\text{DTPA})^{2-}$	630	1.1	[49]
	—	—	$\text{Eu}(\text{DTPA})^{2-}$	560–638	—	[28]
Eu-MS-325	3.6–11.0	579.91	$\text{Eu}(\text{MS-325})^{2-}$	$617 \pm 7$	1.0	This work
	13.0	579.90	$\text{Eu}(\text{MS-325})^{2-}$	$526 \pm 8$	1.3	This work
Eu-HMDTPA	3.6–11.0	579.92	$\text{Eu}(\text{HMDTPA})^{2-}$	$632 \pm 10$	1.0	This work
	13.0	579.91	$\text{Eu}(\text{HMDTPA})^{2-}$	$546 \pm 8$	1.2	This work
Cm-DTPA	3.6–9.0	404.20, 400.32, 396.51	$\text{Cm}(\text{DTPA})^{2-}$	$285 \pm 6$	1.4	This work
	13.0	404.20, 400.20, 396.51	$\text{Cm}(\text{DTPA})^{2-}$	$242 \pm 8$	1.8	This work
	—	—	$\text{Cm}(\text{DTPA})^{2-}$	257	1.65	[5]
Cm-MS-325	3.6–9.0	404.05, 400.32, 396.51	$\text{Cm}(\text{MS-325})^{2-}$	$269 \pm 6$	1.5	This work
	13.0	404.04, 400.25, 396.54	$\text{Cm}(\text{MS-325})^{2-}$	$232 \pm 7$	1.9	This work
Cm-HMDTPA	3.6–9.0	404.04, 400.32, 396.51	$\text{Cm}(\text{HMDTPA})^{2-}$	$271 \pm 7$	1.5	This work
	13.0	404.12, 400.38, 396.78	$\text{Cm}(\text{HMDTPA})^{2-}$	$242 \pm 6$	1.8	This work

in aminopolycarboxylates [5]. The DFT (density functional theory) calculations are also consistent with the presence of nine waters of hydration in the inner coordination shell

of  $\text{Cm}^{3+}$  [19]. The protonated complex of L was also not observed in the present systems as such complexes usually form at  $\text{pH} < 3.0$  [40].



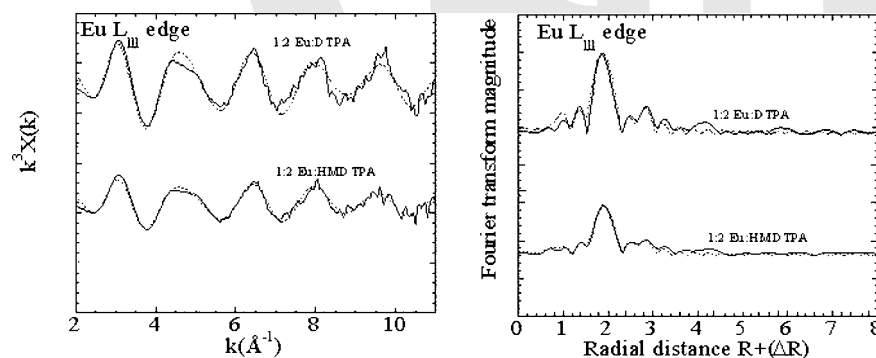
**Fig. 9.** The excitation spectra of  $\text{Eu}^{3+}$  and  $\text{Cm}^{3+}$  complexes with HMDTPA (a)  $\text{Eu}:\text{HMDTPA}$ , 1 : 2, pH = 3.6; (b)  $\text{Eu}:\text{HMDTPA}$ , 1 : 2, pH = 11.5; (c)  $\text{Cm}:\text{HMDTPA}$ , 1 : 2, pH = 3.6 and (d) 1 : 2, pH = 11.5;  $[\text{Eu}^{3+}] = 1 \times 10^{-4} \text{ M}$ ,  $[\text{Cm}^{3+}] = 2 \times 10^{-6} \text{ M}$ ;  $I = 0.10 \text{ M}$  ( $\text{NaClO}_4$ ).

### 3.3 EXAFS studies

The formation and the coordination environment of  $\text{M}^{3+}$  in these complexes were further confirmed by solution EXAFS studies. Fig. 10 shows the fitted and  $k^3$ -weighted ( $2.0\text{--}11.0 \text{ \AA}$ )  $L_{\text{III}}$  edge EXAFS spectra for  $\text{Eu}:\text{DTPA}$  (1 : 2, pH = 6.0),  $\text{Eu}:\text{HMDTPA}$  (1 : 2, pH = 9.3), and their Fourier transformed spectra in de-ionized water. The spectra show similarity both in phase and amplitude, supporting the similarity in the bonding of carboxylates and nitrogens. The best fit data and the corresponding Debye-Waller factors are given in Table 7. The nearest neighbors of Eu in the  $\text{Eu}:\text{DTPA}$  complex are  $5.8 \pm 1.0$  oxygens with  $\text{Eu}\text{--O}$  distances of  $2.40 \pm 0.01 \text{ \AA}$ ,  $2.7 \pm 0.9$  nitrogens at a distance of  $2.81 \pm 0.02 \text{ \AA}$ , and  $4.2 \pm 1.5$  carbons at a distance of  $3.31 \pm 0.02 \text{ \AA}$  (Table 7). The presence of carbon at this

distance identifies it as being associated as a carboxylate group. The EXAFS data analysis (Table 7) confirmed the formation of  $\text{Eu}(\text{DTPA})(\text{H}_2\text{O})^{2-}$  with DTPA binding *via* five carboxylates and three nitrogens which is consistent with the crystallography analysis [2]. In the crystal structure of  $\text{K}_2[\text{Eu}(\text{DTPA})(\text{H}_2\text{O})]$  determined in solid phase by X-ray crystallography [39], the average  $\text{Eu}\text{--O}$  bond distance of  $2.41 \text{ \AA}$  and  $\text{Eu}\text{--N}$  bond distance of  $2.69 \text{ \AA}$  were reported. These bond distances agree well with those measured by solution EXAFS for  $\text{Eu}\text{--DTPA}$  complex. The Eu bonding in the  $\text{Eu}:\text{HMDTPA}$  complex consists of  $5.6 \pm 0.4$  oxygens at a distance of  $2.40 \pm 0.01 \text{ \AA}$ ,  $2.9 \pm 0.4$  nitrogens at  $2.79 \pm 0.02 \text{ \AA}$  and  $3.6 \pm 1.0$  carboxylates carbons at  $3.33 \pm 0.02 \text{ \AA}$ . These data lead to a total coordination number,  $\text{CN} = 8.5$  ( $1\text{HMDTPA}$  (5 carboxylates + 3 nitrogens) +  $1\text{H}_2\text{O}$ ) for  $\text{Eu}^{3+}$  in  $\text{Eu}(\text{HMDTPA})(\text{H}_2\text{O})^{2-}$ . Unfortunately, the solution EXAFS spectra of  $\text{Eu}\text{--MS-325}$  were very inclusive. Despite several attempts, we have not been able to obtain good quality spectra for the  $\text{Eu}\text{--MS-325}$  system.

Geometry optimization of structures of  $\text{La}^{2-}$  complexes were performed in aqueous solution at the DFT (level) by using LANL2DZ basis set. In these calculations second-sphere water molecules were excluded, and solvent effects were included by using the polarizable continuum model (PCM) [41]. The optimized structures and the bond lengths are shown in Fig. 11 and Table 8, respectively. In the structure of  $\text{La}^{2-}$ , the DTPA ligand is octadentate with five oxygen atoms from the carboxylate groups and three nitrogen atoms from the amine groups coordinating to  $\text{La}^{3+}$ . The complex contains one water molecule in the inner coordination sphere of  $\text{La}^{3+}$ , satisfying the total coordination number of 9 (Fig. 11). The oxygen atoms from the carboxylate groups and water are considerably closer to the central La atom ( $\text{La}\text{--O} = 2.520$  to  $2.610 \text{ \AA}$ ) than the nitrogen atoms from the amine groups ( $\text{La}\text{--N} = 2.829$  to  $2.937 \text{ \AA}$ ). Average bond lengths increase in the order:  $\text{La}\text{--O}_{\text{carboxylate}} < \text{La}\text{--O}_{\text{water}} < \text{La}\text{--N}$ , reflecting the preference of lanthanum for hard donors in these strongly ionic bonds. This trend of short  $\text{M}\text{--O}$  bonds and long  $\text{M}\text{--N}$  bonds is seen in a variety of aminopolycarboxylate complexes. For  $\text{Ln}\text{--EDTA}$  complex, it is seen that the average  $\text{Ln}\text{--O}$  bond is  $0.0321 \text{ \AA}$  shorter than that calculated from ionic radii [42], while the average  $\text{Ln}\text{--N}$  bond is  $0.087 \text{ \AA}$  longer than calculated. The  $\text{Ln}(\text{DTPA})^{2-}$  complexes ( $\text{Ln} = \text{Nd}, \text{Eu}, \text{Dy}, \text{Ho}, \text{Er}$  and  $\text{Yb}$ ) also have shown to have shorter  $\text{Ln}\text{--O}$  and longer  $\text{Ln}\text{--N}$  interactions than expected [43]. Using the optimized structure of  $\text{La}(\text{DTPA})^{2-}$  as a starting point, the structures of  $\text{La}(\text{HMDTPA})^{2-}$  were further optimized. The optimized



**Fig. 10.** The fitted  $k^3$ -weighted ( $2.0\text{--}12.0 \text{ \AA}^{-1}$ ) (a) and Fourier transformed spectra (b). Showing association of  $\text{Eu}^{3+}$  with DTPA and HMDTPA. Experimental data (—); fitted data (---).

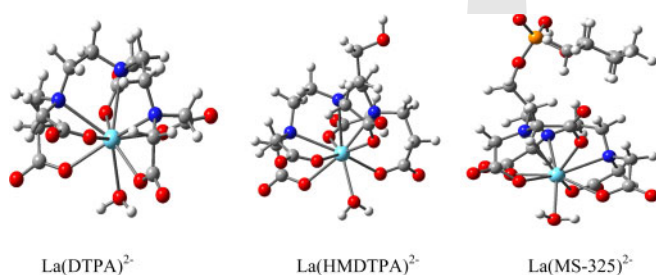
**Table 7.** EXAFS fitting data showing the association of DTPA and HMDTPA with  $\text{Eu}^{3+}$ .

Sample	Atom	N	R (Å)	$\sigma^2$	$E_0$	R
Eu : DTPA, 1 : 2	Eu–O	$5.8 \pm 1.0$	$2.40 \pm 0.01$	$0.008 \pm 0.001$	$2.9 \pm 0.5$	0.050
	Eu–N	$2.7 \pm 0.9$	$2.81 \pm 0.02$	$0.011 \pm 0.002$	$9.7 \pm 0.6$	
	Eu–C	$4.2 \pm 1.5$	$3.31 \pm 0.02$	$0.010 \pm 0.003$	$4.1 \pm 0.4$	
Eu : HMDTPA, 1 : 2	Eu–O	$5.6 \pm 0.4$	$2.40 \pm 0.01$	$0.009 \pm 0.001$	$2.7 \pm 2.4$	0.010
	Eu–N	$2.9 \pm 0.4$	$2.79 \pm 0.02$	$0.014 \pm 0.001$	$7.5 \pm 2.3$	
	Eu–C	$3.6 \pm 1.0$	$3.33 \pm 0.02$	$0.011 \pm 0.001$	$4.2 \pm 1.1$	

N = number of atoms in each coordination shell; R = radial distance between the two atoms of each atomic pair in Angstroms;  $\sigma^2$  = relative mean square displacement from the average path length (Debye–Waller factor);  $E_0$  = energy shift for the photoelectron; R = goodness of fit parameter.

**Table 8.** Calculated Eu–N and Eu–O bond distances (Å) in the  $\text{LaL}^{2-}$  complexes.

Sample	DTPA	MS-325	HMDTPA
La–N <sub>1</sub>	2.937	2.943	2.942
La–N <sub>2</sub>	2.846	2.902	2.848
La–N <sub>3</sub>	2.829	2.837	2.830
La–O <sub>1</sub>	2.533	2.489	2.549
La–O <sub>2</sub>	2.532	2.520	2.529
La–O <sub>3</sub>	2.568	2.564	2.533
La–O <sub>4</sub>	2.543	2.598	2.540
La–O <sub>5</sub>	2.520	2.540	2.543
La–O (water)	2.610	2.620	2.570

**Fig. 11.** Optimized structures of the octadentate  $\text{La}(\text{DTPA})^{2-}$ ,  $\text{La}(\text{MS-325})^{2-}$  and  $\text{La}(\text{HMDTPA})^{2-}$  complexes. Atom: Aqua = La; red = oxygen; blue = nitrogen; gray = carbon; white = hydrogen.

structures and the calculated bond lengths are shown in Fig. 11 and Table 8. The structural features of these complexes are the same as that of  $\text{La}(\text{DTPA})^{2-}$ . In  $\text{La}(\text{MS-325})^{2-}$  complex, the average La–O and La–N distances become longer compared to La–O and La–N distances in  $\text{La}(\text{DTPA})^{2-}$  and  $\text{La}(\text{HMDTPA})^{2-}$ , indicating weakening of these two coordination. However, all three nitrogen atoms and five oxygen atoms remain coordinated with La, and the MS-325 ligand is still octadentate in the  $\text{La}(\text{MS-325})^{2-}$  complex.

## 4. Conclusion

This study provides some new data and understanding of the formation and coordination modes of the trivalent lanthanides and actinides complexes with DTPA derivative ligands. The ligands, DTPA, MS-325, and HMDTPA act as an octadentate ligands binding *via* five carboxylates oxygen and three nitrogen atoms upon complexation with  $\text{Ln}^{3+}$  and  $\text{An}^{3+}$  ions. Luminescence lifetime data indicates that 1 : 1 complex has one residual water of hydration remaining

attached to the  $\text{M}^{3+}$ . The distribution measurement studies of  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$  and  $\text{Eu}^{3+}$  with L in 0.10 M ( $\text{NaClO}_4$ ) also support the formation of 1 : 1 complex in the temperature range 0–45 °C. The complexation is exothermic and becomes weaker as the temperature is increased. The complexation strength of these ligands follows the order:  $\text{DTPA} \approx \text{HMDTPA} > \text{MS-325}$  indicating steric effect of the bulky substituents constraining the ligands into a chelation in the MS-325 complex. The octadentate ligands MS-325 and HMDTPA form thermodynamically stable  $\text{Gd}^{3+}$  complexes in aqueous solution, and can be considered as new basic structural frameworks for the design of novel MRI. The calculated structures for the  $\text{La}^{3+}$  complexes are in reasonably good agreement with the experimental solution structures. The computational approach presented in this work, in combination with experimental information obtained by distribution measurements, luminescence and EXAFS spectral studies, provides structural as well as coordination properties of these complexes in solution.

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